DOI:
10.1063/1.1818742

Document Version
Publisher's PDF, also known as Version of record

Scanning probe energy loss spectroscopy below 50 nm resolution

F. Festy[a] and R. E. Palmer[b]
Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, Birmingham B15 2TT, United Kingdom

(Received 9 February 2004; accepted 24 September 2004)

We report scanning probe energy loss spectroscopy (SPELS) measurements from a roughened Si(111) surface in ultrahigh vacuum. The experiments, which utilize a scanning tunneling microscope tip in the field emission mode as the electron source, establish that the spatial resolution in SPELS is better than 50 nm. The spectral maps acquired indicate different contrast mechanisms for the inelastically scattered and secondary electrons identified in the energy loss spectrum. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1818742]

Electron energy-loss spectroscopy (EELS) in reflection mode is a valuable probe of surface excitations, covering a wide range from the vibrational regime out to electronic excitations such as interband transitions and plasmons.[1,2] Scanning probe energy-loss spectroscopy (SPELS) is a new technique[3] which aims to acquire such energy-loss spectra in a spatially resolved fashion. The tip of a scanning tunnel microscope (STM) is operated in the field emission mode to generate a local electron flux, which can be scattered from the surface and collected by a conventional electron energy analyzer. The energy resolution available from a standard metal tip (replacing the monochromator in EELS) is ~0.3 eV, so the technique is best suited to the acquisition of electronic excitation spectra. Recent reports[3–5] have focused on the information content of the SPELS spectra, demonstrating plasmon modes and interband excitations akin to conventional EELS. An obvious question now is, "What is the spatial resolution of the technique?" Simulations[4] indicate that, at least in the case of a well-screened tip, a spatial resolution on the order of 10–20 nm and, indeed, approaching 1 nm (if the detected signal is angle resolved) may be possible. The ultimate spatial resolution appears to be much smaller than the diameter of the spot irradiated by the tip, since electrons incident at the edge of the spot can more easily escape from the strong tip field and reach the analyzer. In this Letter we report an experimental approach to this question. In particular, we obtain spectral maps of a (roughened) Si(111) surface that establish an upper limit of 50 nm for the spatial resolution in SPELS.

The SPELS instrument employed in this study employed a STM head based on the "pocket size" STM design of Lyding and others,[6–8] which provides good access to the sample surface. The STM tips were produced by etching a 0.5 mm polycrystalline tungsten wire in a two-molar solution of NaOH; the tips were cleaned *in situ* by electron bombardment heating, and sharpened by argon ion sputtering. The tips were checked with a scanning electron microscope and exhibited a sharp apex with a radius of 10–20 nm. The electron analyzer used to collect the backscattered electrons was a miniature four-grid retarding field analyzer (RFA), with a 2-mm entrance aperture positioned 25 mm away from the tip-surface junction. The RFA analyzer, chosen because of its high throughput, was mounted parallel to the surface, where the signal levels in SPELS are highest.[3] The energy resolution of the analyzer was ~0.1 eV.[9,10]

The test sample in the experiments was a Si(111) surface, cleaned in ultrahigh vacuum (UHV) by electron bombardment heating at 1250 °C. The surface was deliberately roughened by heating in a pressure of 10^{-8} mbar (predominantly hydrogen) in order to generate surface texture on the 10–100 nm scale, as confirmed by conventional STM imaging with the tip. The SPELS experiments employed a tip-bias voltage of −120 V and a field emission sample current of 20 nA. Under these conditions, the tip-sample separation is ~100 nm.

The data were acquired by repeated scanning of the same surface area (500×500 nm) with a series of retarding voltages on the analyzer. The RFA acts as a high pass filter. By subtracting images of the backscattered electrons acquired with two different retarding voltages, one can also acquire a spatial map of all the electrons detected within a given energy-loss range. Moreover, since the sample current was kept constant by adjusting the tip-sample distance during a scan, a topographic map of the surface was obtained in parallel with every backscattered image.

Figure 1 shows a series of images obtained from the same area of the roughened Si(111) surface. Figures 1(a)–1(f) were each obtained by subtracting images acquired with successive retarding voltages, as explained above. The range of electron kinetic energies that each represents is labeled in the figure. Note that the tip-bias voltage was −120 V, so assuming a tip-work function of ~5 eV the incident electron energy in these experiments is ~115 eV [thus Fig. 1(a) represents the energy-loss range from 5 eV to −5 eV about the elastic peak]. As we pass from Fig. 1(a) to Fig. 1(f) we are looking at electrons of decreasing kinetic energy, i.e., we are moving from the elastic peak region of the spectrum through the energy-loss features associated with plasmon and interband excitations[11–17] until we finally reach the low-energy secondary electrons emitted from the surface. We have previously reported images[6,18] in which the total yield of backscattered (and secondary) electrons was recorded while scanning across the surface, and shown that in this case the image contrast depends on shadowing effects and edge enhancement arising from the surface topography.[18] The individual images shown in Fig. 1 can be summed together to produce such a total electron image; thus also la-

[a]Present address: Physics Dept., King's College London, Strand, London WC2R 2LS.
[b]Author to whom correspondence should be addressed; electronic mail: R.E.Palmer@bham.ac.uk

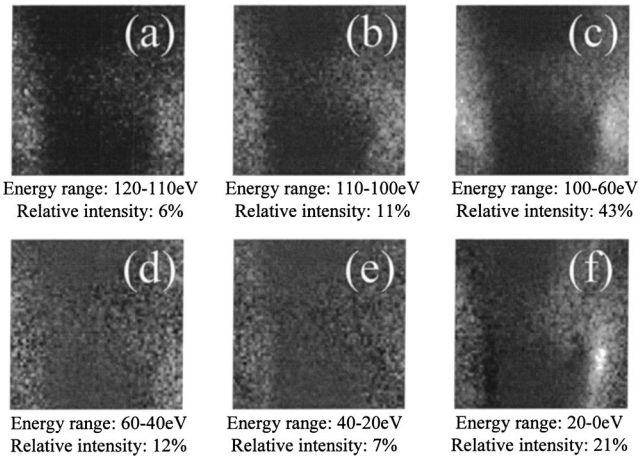

FIG. 1. Electron energy-loss images (500 nm×500 nm) from the roughened Si(111) surface, obtained by subtracting spectra acquired with different retarding voltages. (a) $-5\ \text{eV} < E_{\text{loss}} < 5\ \text{eV}$ (elastic peak). (b) $5\ \text{eV} < E_{\text{loss}} < 15\ \text{eV}$ (surface plasmon). (c) $15\ \text{eV} < E_{\text{loss}} < 55\ \text{eV}$ (bulk plasmon, contamination, multiple excitations). (d) $55\ \text{eV} < E_{\text{loss}} < 75\ \text{eV}$ (multiple excitations). (e) $20\ \text{eV} < E_{\text{kinetic}} < 40\ \text{eV}$ (high-energy secondary electrons), and (f) $0\ \text{eV} < E_{\text{kinetic}} < 20\ \text{eV}$ (low-energy secondary electrons).

beled in Fig. 1 is the percentage of the total electron signal contributed by each range of energies. We then see, for example, that the low energy secondary electrons (kinetic energy range 0–20 eV) contribute only 21% of the total backscattered signal, while the inelastically scattered electrons with kinetic energies from 40 to 110 eV, i.e., the sum of Figs. 1(b)–1(d), contribute 66%.

Comparison of the various images shown in Fig. 1 reveals an obvious similarity at the broad level, reflecting the topography of the roughened surface, but also differences in detail, e.g., compare Fig. 1(d) with Fig. 1(f). Detailed inspection of particular images reveals features that can be resolved on the length scale of 10–20 nm [see, for example, the bright spots on the left-hand side of Fig. 1(c) and the bright ridge on the lower right of Fig. 1(f)]. This allows us to obtain a spatial resolution within the energy loss images of 10–20 nm, at least comparable with and possibly somewhat better than the resolution of 20–30 nm reported previously from the total electron images.[18]

Of particular interest in potential applications of the SPELS technique is the length scale over which distinctly different energy-loss spectra can be obtained. From a set of energy-resolved images, such as those shown in Fig. 1, we can obtain a two-dimensional set of electron spectra, where each energy-loss spectrum corresponds to a particular location on the surface. In order to obtain this spectral map, the imaging area of Fig. 1 (500×500 nm) was divided up into squares of size 50×50 nm. This pixel size was chosen to be larger than that in the spatial images to allow for signal averaging across all the original pixels in each 50×50 nm square. Since the images of Fig. 1 were acquired with a discrete set of retarding voltages, the local spectra obtained in this case represent the electron energy-loss signals obtained within certain bands of energy. They are shown in Fig. 2. The colored blocks in each spectrum correspond to the sequence of energy-loss ranges in Fig. 1. The height of each block gives the number of electrons detected per unit range of energy loss. The crucial question for the present purpose is whether the spectra from adjacent 50×50-nm surface regions can be distinguished. Inspection of Fig. 2 shows

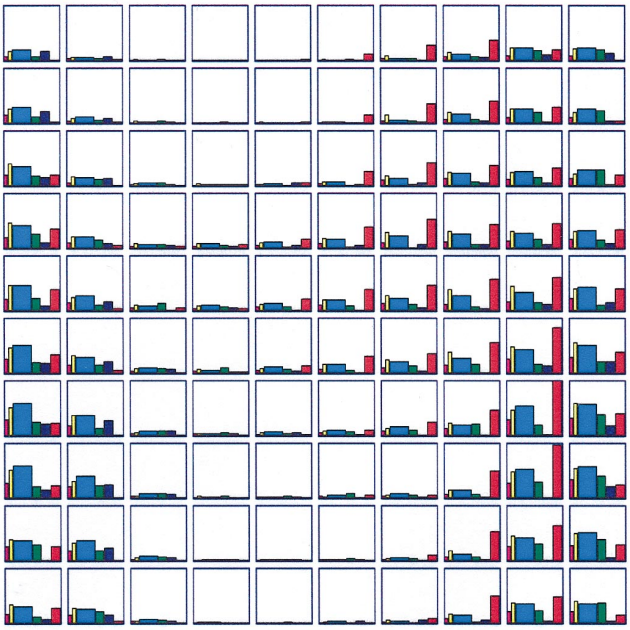

FIG. 2. (Color) Two-dimensional spectral map of the silicon surface imaged in Fig. 1. Each spectrum corresponds to a 50 nm×50 nm square on the surface. The spectra are composed of six energy bands, matching the spectral ranges given in Fig. 1.

clearly that this is the case, as revealed, for example, by comparison between the height of the blue (inelastic scattering) and red (secondary electron) blocks. We conclude that distinct, local energy-loss spectra can be acquired with the SPELS technique with a spatial resolution of better than 50 nm.

In this letter we have reported measurements of the spatial resolution which can be achieved in scanning probe energy-loss spectroscopy (SPELS). Local energy-loss spectra, obtained by the subtraction of images acquired with a retarding field analyzer, are distinguishable on a scale of at most 50 nm. Energy-resolved images of the surface reveal measurable features on the length scale 10–20 nm. This is an innovation in a branch of science (field emission from a metal tip) which dates back[3–5,19,20] at least 30 years. The measurements demonstrate that SPELS has the potential to probe the excited states of surface structures, and thus also provide chemical analysis, on the scale of 10–50 nm (and possibly below).

We thank the Paul Fund of the Royal Society for support of this work. F.F. is grateful to the University of Birmingham for studentship support.

[1]H. Raether, *Excitation of Plasmon and Interband Transitions by Electrons* (Springer-Verlag, Berlin 1980); A. Liebsh, *Electronic Excitations at Metal Surfaces* (Plenum Press, New York, 1997).
[2]Y. Chen, J.C. Barnard, R.E. Palmer, M.O. Watanabe, and T. Sasaki, Phys. Rev. Lett. **83**, 2406 (1999); Z.Y. Li, M.R.C. Hunt, and R.E. Palmer, Surf. Sci. **352**, 442 (1996); C.M. Grimaud, L. Siller, M. Andersson, and R.E. Palmer, Phys. Rev. B **59**, 9874 (1999).
[3]B.J. Eves, F. Festy, K. Svensson, and R.E. Palmer, Appl. Phys. Lett. **77**, 4223 (2000).
[4]R.E. Palmer, B.J. Eves, F. Festy, and K. Svensson, Surf. Sci. **502**, 224 (2002).
[5]R.E. Palmer, Surf. Interface Anal. **34**, 3 (2002).
[6]J.W. Lyding, S. Skala, J.S. Hubacek, and R. Brockenbrough, Rev. Sci. Instrum. **59**, 1897 (1988).
[7]G.F.A. van de Walle, J.W. Gerritsen, H. Van Kempen, and P. Wyder, Rev.

Sci. Instrum. **56**, 1573 (1985).
[8]R.T. Brockenbrough and J.W. Lyding, Rev. Sci. Instrum. **64**, 2225 (1993).
[9]F. Festy Ph.D. thesis, The University of Birmingham, 2000.
[10]N.J. Taylor, Rev. Sci. Instrum. **40**, 793 (1969).
[11]U. Del Pennino, P. Sassaroli, and S. Valeri, Surf. Sci. **122**, 307 (1982).
[12]N. Aoto, E. Ikawa, and Y. Kurogi, Surf. Sci. **199**, 408 (1988).
[13]P. Perfetti, S. Nannarone, and A. Savoia, Phys. Rev. B **26**, 1125 (1982).
[14]N. Ishimaru, H. Ueba, and C. Tatsuyama, Surf. Sci. **193**, 193 (1988).
[15]J.E. Rowe and H. Ibach, Phys. Rev. Lett. **31**, 102 (1973).
[16]G.B. Hoflund, S. Mitamura, M. Davidson, and H. Yoneyama, J. Phys.: Condens. Matter **5**, A149 (1993).
[17]J. Stiebling and H. Raether, Phys. Rev. Lett. **40**, 1293 (1978).
[18]F. Festy, K. Svensson, P. Laitenberger, and R.E. Palmer, J. Phys. D **34**, 1849 (2001).
[19]R.D. Young, Phys. Today **24**, 42 (1971); B. Reihl and J.K. Gimzewski, Surf. Sci. **189**, 36 (1987); H.W. Fink, Phys. Scr. **38**, 260 (1988).
[20]R. Allenspach and A. Bischof, Appl. Phys. Lett. **54**, 587 (1989); J. Frohn, Ph.D. thesis, RWTH Aachen, 1992; M. Tomitori, H. Terai, and T. Arai, Appl. Surf. Sci. **145**, 123 (1999).